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Application of the Pitzer model for the estimation of activity coefficients of electrolytes in ion selective membranes

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Abstract

The Pitzer model can be applied to predict the mean activity coefficients of salts in aqueous electrolyte solutions as a function of the molality. In this work it is shown that the mean activity coefficients for NaOH and NaCl solutions as predicted by the Pitzer model are in good agreement with experimental data from literature. Hereafter, the Pitzer model was extended to the description of the activity coefficients in ion selective membranes. Experimental sorption data of NaOH and NaCl obtained for sulfonic DuPont membranes with $EW_{dry} = 1.10$ and 1.50, respectively, were used to determine the Pitzer parameters describing the interaction between the fixed charged groups of the membrane and the other ions dissolved in the membrane. In the application of the Pitzer model to the membrane, it was assumed that the fixed charged groups of the membrane can be considered as 'ordinary' ions evenly distributed in the aqueous solution inside the membrane. The results indicate that the Pitzer model can be used to describe the experimental mean activity coefficients in sulfonic DuPont membranes, provided the molality of the membrane, as used in the Pitzer relations, is multiplied by a constant representing a shielding term. This shielding term, $f_{shielding}$, is a scaling factor depending on the equivalent weight.

Keywords: Activity coefficient; Chemical potential; Pitzer model; Ion selective membranes

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1. Introduction

Activity coefficients of electrolytes dissolved in water are a special subject of study in the electrochemical literature. For electrolytes dissolved in water, it is possible to predict the activity coefficient of the single ions with the help of the various (semi-empirical) models presented in literature (e.g., the (extended) Debye–Hückel or the Pitzer model [1]). For studies involving ion-selective membranes, it is often difficult to predict the activity coefficients of the ions inside these membranes. However, these activity coefficients are necessary for the calculation of the electrochemical potential which is a very important parameter in electrochemical studies. If the electrochemical potential can be calculated, it is, for example, possible to determine the thermodynamic equilibrium sorption of ions in ion exchange resins or in ion-selective membranes.

The electrochemical potential is also important in mass transfer processes in ion-selective membranes as encountered in, e.g., chloralkali electrolysis processes (see, e.g., Ref. [2]). The membranes which are used in the chloralkali electrolysis processes are composite membranes (like Nafion or Asahi Glass membranes) and consist of two or even three separate ion-selective layers. These layers can be different with respect to the kind of active groups (carboxylic or sulfonic), the molality of the active groups (the so-called Equivalent Weight [= kg dry polymer per mole fixed charged groups]) and, of course, the thickness of the layers. Usually in mass transfer processes, it is assumed that not only at the liquid–membrane interfaces but also at the membrane–membrane interfaces thermodynamic equilibrium is established meaning that the electrochemical potential at both sides of the interface is identical. Furthermore, in a mass transfer process, the driving force for mass transport is represented by the gradient in the electrochemical potential.

From the argumentation above, it will be clear that a reliable estimation of the sorption of ions in ion-selective membranes or ion exchange resins, or the prediction of any mass transfer phenomenon in ion selective membranes as occurring in, e.g., the chloralkali electrolysis process, is only possible if the estimation of the electrochemical potential, and thus also the activity coefficient, is reliable.

If activity coefficients are applied in a mass transfer model (or in any other study), it is often implicitly assumed that the Gibbs–Duhem relation is satisfied. Therefore, any method or model used for the calculation of the activity coefficients in membranes should also satisfy the Gibbs-Duhem relation (i.e., $\sum_{i=1}^{n} n_i \mathrm{d}\mu_i = 0$).

A general model that describes the activity coefficients as a function of the concentration of ions in aqueous electrolyte solutions is the Pitzer model [1]. This model can be applied for diluted and concentrated aqueous electrolyte solutions and, generally, the predicted mean activity coefficients agree well with experimental data (see, e.g., [3]). Of course, as experiments only yield mean activity coefficients, no statements can be made about the reliability of the predicted individual ion activity coefficients. The main disadvantage of a model like the Pitzer model is that the calculation of the activity coefficients is quite elaborate, and that component-dependent interaction parameters are necessary for the calculation of the activity coefficients. Up to now the Pitzer model has been applied successfully to aqueous electrolyte solutions for which many of these component-dependent interaction parameters have been derived and tabulated (see, e.g., Ref. [1]). However, no publications have appeared in literature which apply the Pitzer model to membranes in order to describe the thermodynamics. In this work, experimental sorption data for sulfonic DuPont membranes are reported, and it is shown that these data can be described satisfactorily by the Pitzer model.

2. Pitzer model

2.1. Application of the Pitzer model to aqueous solutions

Although the Pitzer relations are quite complex (see Appendix A), the application of the Pitzer model results in the determination of individual activity coefficients as a function of the composition of an aqueous electrolyte solution. For an aqueous solution containing n different ions each having a molality of m_i, the Pitzer model states that:

$$\gamma_i = \text{Pitzer relation}_i\ (m_1 \ldots m_n) \tag{1}$$

In the Pitzer relation, the interaction of all ions present in the solution is incorporated by means of concentration-independent interaction coefficients. This means that for an arbitrary composition of an aqueous electrolyte mixture, the activities of all ions present can be estimated with the Pitzer model if the (empirically derived) interaction coefficients are known. The values of these interaction coefficients have been determined for many ions and are tabulated in literature (see, e.g., Ref. [1]).

2.2. Application of the Pitzer model to the membrane

If a membrane is contacted with an aqueous solution, the membrane will take up water and solutes. If the membrane, with its dissolved water and solutes, is considered as an 'aqueous solution', the fixed charged groups of the membrane can also be considered as ions, present in the aqueous solution. As a consequence, this would mean that the Pitzer model may be applicable to the membrane. In this approach, the fixed charged groups of the membrane are considered as 'ordinary' ions evenly distributed in the aqueous solution. However, this is, of course, not true on a micro scale because the charged groups of the membrane are fixed to the matrix and will suffer a kind of shielding from the other ions in the solution. Therefore, if the Pitzer model is applied to the membrane, it seems logical to introduce one extra parameter in the Pitzer relations representing the shielding ($f_{\text{shielding}}$). Therewith, the activity coefficient in the membrane is expressed by:

$$\gamma_i = \text{Pitzer relation}_i\ \left(\overline{m_1} \ldots \overline{m_n}, m_{\text{membrane}}, f_{\text{shielding}}\right)\quad i = 1 \ldots n \tag{2}$$

In the present work, it is further assumed that there are no (crystalline) areas in the membrane which are not accessible to the liquid, which means that:

$$\sum_{i=1}^{n} z_i \overline{m_i} + z_{\text{membrane}} m_{\text{membrane}} = 0 \tag{3}$$

The molality of the fixed charged groups in the membrane (= moles of fixed charged groups per kg water in the membrane) which has to be used in relation (2) and (3) can be calculated with:

$$m_{\text{membrane}} = \frac{\rho_{\text{polymer}}}{\rho_{\text{solvent}} \text{EW}_{\text{dry}}} \frac{1-e}{e} \tag{4}$$

The main problem in applying the Pitzer model to the membrane phase is that the values of interaction coefficients of the fixed charged groups of the membrane with the dissolved ions, necessary in the Pitzer model, have not been presented in open literature. Therefore, these Pitzer interaction parameters have to be determined experimentally. Once the Pitzer parameters are known, the activity coefficients and therewith the corresponding electrochemical potential can be predicted. In this work, it will be shown that the Pizer model can be applied to a membrane by the determination of the Pitzer parameters for a sulfonic DuPont membrane with $EW_{dry} = 1.10$ and $EW_{dry} = 1.50$.

3. Determination of activity coefficients inside the membrane

3.1. Theory

If a membrane is contacted with an aqueous electrolyte solution containing n ionic components and equilibrium is established, the electrochemical potential of all components inside and outside the membrane is identical:

$$\mu_i = \overline{\mu_i} \qquad \text{for } i = 1 \ldots n \text{ and } i = \text{water} \tag{5}$$

With the general definition of the electrochemical potential of the ions

$$\mu_i = \mu_i^0 + RT \ln(m_i \gamma_i) + z_i F \varphi \tag{6}$$

and the assumption that the reference state for both phases is equal ($\mu_i^0 = \overline{\mu_i^0}$), it can be derived for the ions that:

$$\overline{\varphi} - \varphi = \varphi_{\text{Donnan}} = RT \ln \frac{m_i \gamma_i}{\overline{m_i \gamma_i}} \tag{7}$$

The electrochemical potential for water is given by:

$$\mu_w = \mu_w^0 + RT \ln(a_w) = \mu_0^w - \text{RTM}_{\text{solvent}} \phi_{\text{osmotic}} \sum_i m_i \tag{8}$$

with the osmotic coefficient defined as:

$$\phi_{\text{osmotic}} = -\frac{\ln(a_{\text{solvent}})}{M_{\text{solvent}} \sum_i m_i} \tag{9}$$

which means that at equilibrium and the assumption that $\mu_{\text{water}}^0 = \overline{\mu_{\text{water}}^0}$

$$\phi_{\text{osmotic}} \sum_i m_i = \overline{\phi_{\text{osmotic}}} \sum_i \overline{m_i} \tag{10}$$

For an aqueous solution of a given composition the molalities m_i are known, while the activity coefficients and the osmotic coefficient in the aqueous solution can be estimated with the Pitzer

Table 1
Sorption of Cl^- in the membrane from a NaCl-solution (sorption of Cl expressed in μg)

Concentration NaCl (external solution) (mol/l)	DuPont sulfonic EW = 1.10 mass = 356 mg	DuPont sulfonic EW = 1.50 mass = 850 mg
5	6347	921
4	4780	653
3	3783	559
2	2605	312
1	1111	188

parameters given in literature. If the Pitzer parameters describing the interaction between the dissolved ions and the fixed charged groups of the membrane are also known, the molalities of the ions inside the membrane can be predicted, provided there is one extra equation which assures electroneutrality. As already mentioned, in the present work, it is assumed that there are no (crystalline) areas in the membrane that are not accessible to the liquid, which means that the electroneutrality condition is defined by relation (3). If the Pitzer parameters describing the interactions of the fixed charged groups of the membrane with the other ions in the membrane are not known, sorption data can be used to estimate the unknown activity coefficients (and osmotic coefficient) and therewith these unknown Pitzer parameters.

3.2. Experimental procedure and results for the sorption experiments

Two sulfonic membranes were purchased from DuPont and had an $EW_{dry} = 1.10$ and 1.50. These sulfonic membranes were used in the sorption experiments and similar to the sulfonic layers in the Nafion membranes of DuPont. A piece of the sulfonic membrane with a surface area of about 54×10^{-4} m^2 was prior to use in the sorption experiments consecutively contacted with a 6 N NaOH solution and a 2 N HCl solution for three times. Hereafter, the membrane was thoroughly washed and dried at 90°C after which the mass of the membrane was determined. The sorption experiments were

Table 2
Sorption of OH^- in the membrane from a NaOH-solution (sorption of OH expressed in μg)

Concentration NaOH (external solution) (mol/l)	DuPont sulfonic EW = 1.10 mass = 356 mg	DuPont sulfonic EW = 1.50 mass = 850 mg
5	6977 and 6213	993 and 810
4	5200	988
3	3746	642
2	3259	494
1	2284 and 1653	324 and 289

Table 3
Sorption of Cl^- and OH^- in the membrane from a NaCl/NaOH solution (sorption of Cl^- and OH^- expressed in μg)

Concentration NaOH (external solution) (mol/l)	DuPont sulfonic EW = 1.10 mass = 356 mg		DuPont sulfonic EW = 1.50 mass = 850 mg	
	Cl^-	OH^-	OH^-	Cl^-
3	3747	1579	270	553
2	3727	1097	165	522
1	3555	567	< 100	600
0.1	3663	< 100	< 100	564

NaCl concentration of the external solution 3 mol/l.

carried out at 90°C, by contacting the membrane with 50 ml of an aqueous electrolyte solution containing a known amount of NaCl and/or NaOH for 60 h. Because the sorption was small compared to the amount of ions in the aqueous solution, the change in concentration in the liquid was negligible. After 60 h, the membrane was washed with water to remove adhered solution. At 70°C, the membrane was contacted with an excess water for 7 h in order to remove the ions from the membrane. The resulting aqueous solution was analysed on the contents of Cl^- by ion chromatography. The contents of OH^- was determined by acid–base titration. After washing the membrane for a prolonged time with water, the membrane was re-used in subsequent sorption experiments. The results of the experiments are given in Tables 1–3. As it can be in Table 2, it seems that the deviation in the sorption data is about 10–15%. For the determination of the molality of the fixed charged group of the membrane as required in the Pitzer relations, it is necessary to know the water uptake e (see also Eq. (4)). Van der Stegen [4] has measured the water-uptake for sulfonic membranes and has proposed the following correlation:

$$e = 0.6455 + 0.6044\,a_w + 0.1125\,a_w^2 - 0.935\mathrm{EW}_{dry} + 0.36\mathrm{EW}_{dry}^2 - 0.44151\,a_w\mathrm{EW}_{dry} \quad (11)$$

Because the composition of the aqueous solution the membrane was contacted with is known, the required water activity in Eq. (11) can be calculated with the Pitzer parameters given in literature (see, e.g., [1] and Appendix B).

With the water-uptake and the sorption data of OH^- and Cl^-, it is now also possible to calculate the molality of the anions inside the membrane. The molality of Na^+ inside the membrane was not based on experimental sorption data, but derived from the aforementioned condition of electroneutrality inside the membrane:

$$z_{Na^+}\overline{m_{Na^+}} = \sum_{i = Cl^-, OH^-} z_i\,\overline{m_i} + z_m m_m \quad (12)$$

4. Activity coefficients in aqueous solutions

Before the Pitzer model was applied to the membrane, it was determined if the Pitzer model is suitable to predict the activity coefficients in aqueous NaCl or NaOH containing solutions. The Pitzer

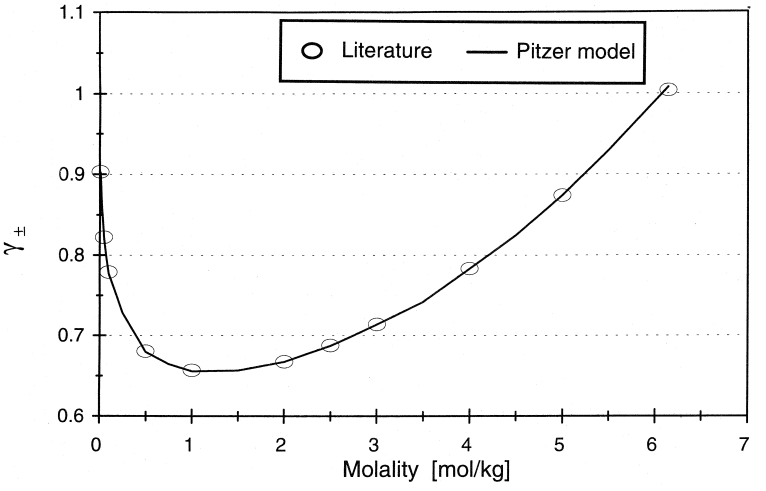

Fig. 1. Comparison of theoretical and experimental mean activity coefficient of NaCl in an aqueous NaCl solution as a function of the molality at 25°C.

parameters as used in the calculations were obtained from Pitzer [1] and are summarized in Appendix B. In Figs. 1–3, the calculated mean activity coefficients are compared to experimental data from literature [5].

From the results in Figs. 1 and 2, it can be concluded that the Pitzer model predicts the mean activity coefficients of single salts dissolved in water very well. For the prediction of the mean

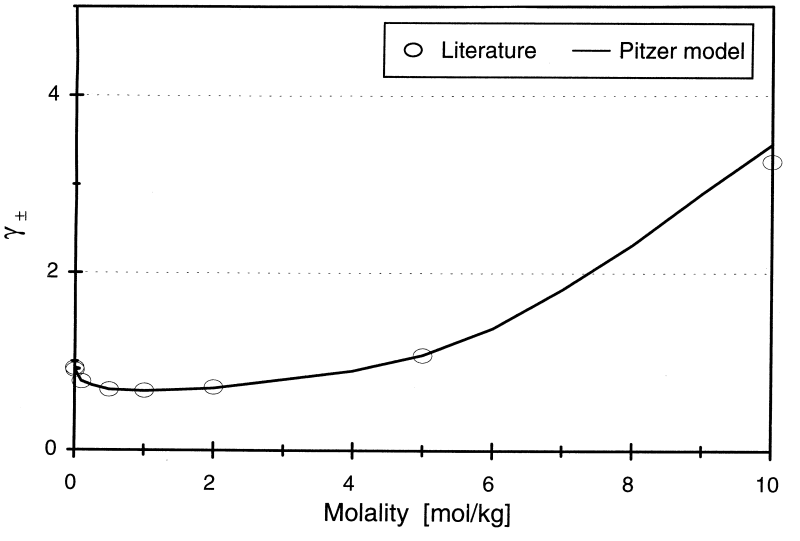

Fig. 2. Comparison of theoretical and experimental mean activity coefficient of NaOH in an aqueous NaOH solution as a function of the molality at 25°C.

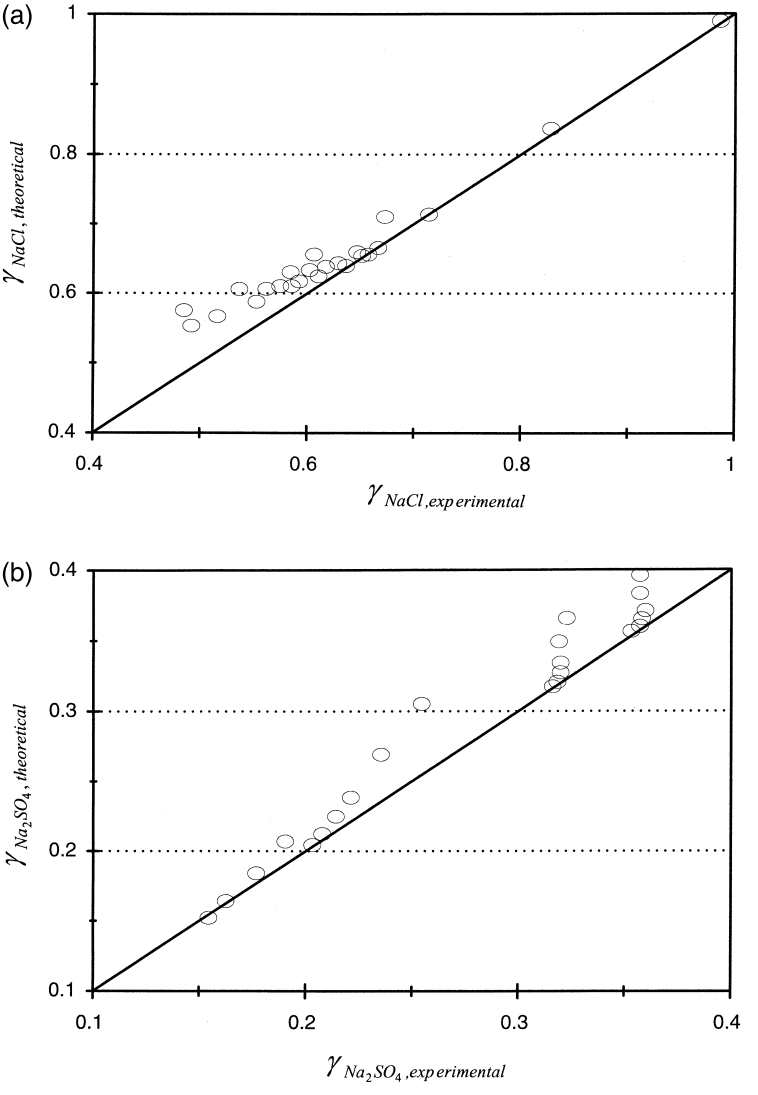

Fig. 3. Comparison of the calculated and the literature mean activity coefficients of NaCl (graph 3a) and Na_2SO_4 (graph 3b) in a mixture of NaCl and Na_2SO_4 at various concentrations of NaCl and Na_2SO_4 at 25°C. The mean activity coefficient is defined as $\gamma_{\pm} = (\gamma_+^{\nu_+} \gamma_-^{\nu_-})^{\frac{1}{\nu}}$.

activity coefficients of an electrolyte in mixtures of electrolytes the Pitzer model can also be applied, which is illustrated in Fig. 3 for the $NaCl/Na_2SO_4$ system. The deviations between calculated and literature values of the mean activity coefficients are in this case at maximum 20%. The largest deviations are obtained for systems where one salt is present in a low concentration and the other salt in a high concentration. The mean activity coefficient of the salt with the high concentration is predicted accurately by the Pitzer model, but the estimated mean activity coefficient of the salt present in a low concentration shows a relatively large deviation from the (experimental) literature values. A

reasonable explanation is that the experimental accuracy of the determination of the mean activity coefficient of a salt present in low concentrations in mixed electrolyte systems is relatively low.

Overall, it can be concluded that the results obtained with the Pitzer model for an aqueous solution as encountered in chloralkali electrolysis processes are satisfactory.

5. Application of the Pitzer model to the membrane

For the sulfonic DuPont membrane with $EW_{dry} = 1.10$, the Pitzer parameters describing the interaction between the fixed charged groups of the membrane and the dissolved ions were determined by fitting the predicted sorption data of the Pitzer model to the experimental sorption data (see Section 3.2 for the experimental determination of the sorption data) minimizing the following target function SS:

$$SS = \sum_{i=i}^{n} \left(m_{i,\text{exp}} - m_{i,\text{ theoretical Pitzer model}} \right)^2 \tag{13}$$

In this procedure, the interaction between the dissolved ions needed for the calculation of $m_{i,\text{theoretical Pitzer model}}$ was described by the Pitzer interaction coefficients as they can be found in literature (see Refs. [1,5], see Appendix B for a summary of the data used). The shielding of the fixed charged groups of the membrane from the other dissolved ions was accounted for by multiplying the molality of the charged groups in the membrane by the shielding factor ($f_{\text{shielding}}$) in the Pitzer relations. Because the shielding factor, $f_{\text{shielding}}$, is unknown and cannot be measured experimentally, this factor was given a reference value of 1 for the sulfonic DuPont membrane with $EW_{dry} = 1.10$. This way, possible effects of shielding will automatically be incorporated in the set of Pitzer parameters which was determined for this membrane. In the optimization procedure, the Pitzer interaction coefficients between the fixed charged groups of the membrane, and the dissolved ions were determined using the experimental sorption data and the method as described in Section 3.1. The resulting parameters from the optimization procedure describing the interaction between the membrane charged groups and the dissolved ions are given in Table 4.

Table 4
Pitzer interaction parameters at 90° C for the sulfonic DuPont membrane (see also Appendix A for the Pitzer equations)

Interaction parameter	Value
$\beta^{(0)}_{\text{Na+, membrane}}$	0.07031
$\beta^{(1)}_{\text{Na+, membrane}}$	−11.0268
$C^{\phi}_{\text{Na+, membrane}}$	−0.00362
$\phi_{\text{Cl−, membrane}}$	0.28584
$\Psi_{\text{Na+, Cl−,membrane}}$	−0.04446
$\phi_{\text{OH−, membrane}}$	0.17011
$\Psi_{\text{Na+, OH−,membrane}}$	−0.01134

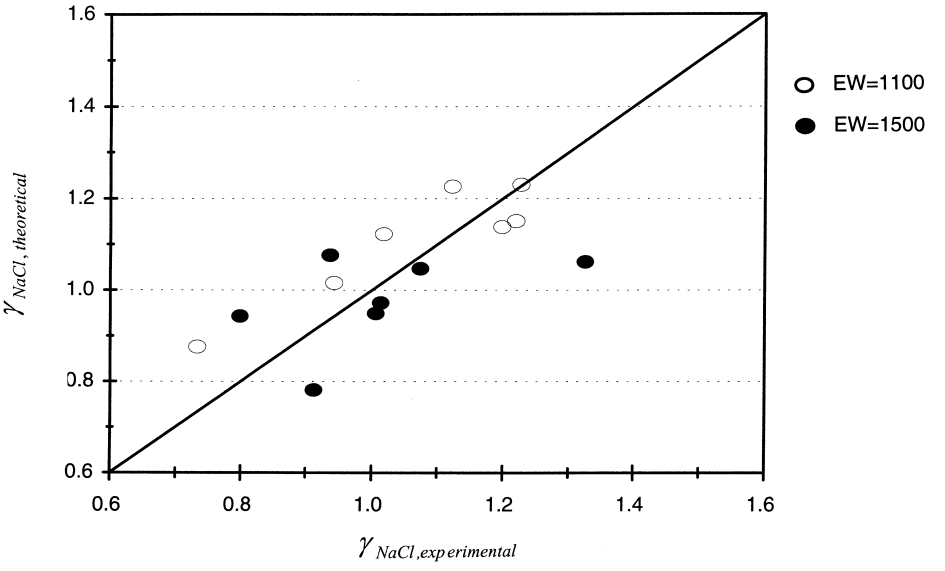

Fig. 4. Comparison of theoretical and experimental mean γ_{NaCl} in sulfonic DuPont membranes at 90°C.

The final results in terms of activity coefficients and water activity are given in Figs. 4–6 by the open points. As can be seen in these figures the Pitzer model is able to describe the experimental data very reasonably. If the same set of Pitzer parameters with $f_{shielding} = 1$ was applied to the sulfonic

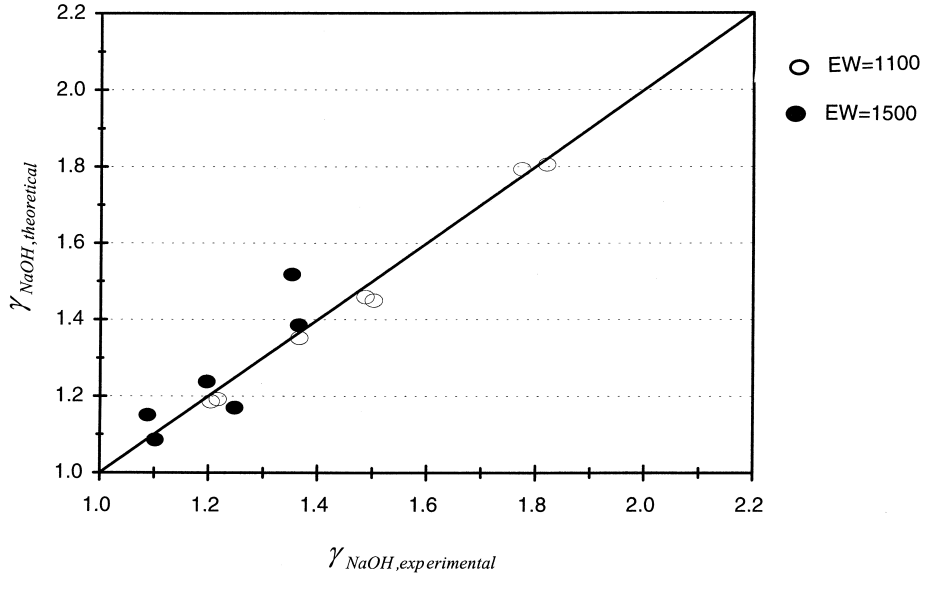

Fig. 5. Comparison of theoretical and experimental mean γ_{NaOH} in sulfonic DuPont membranes at 90°C.

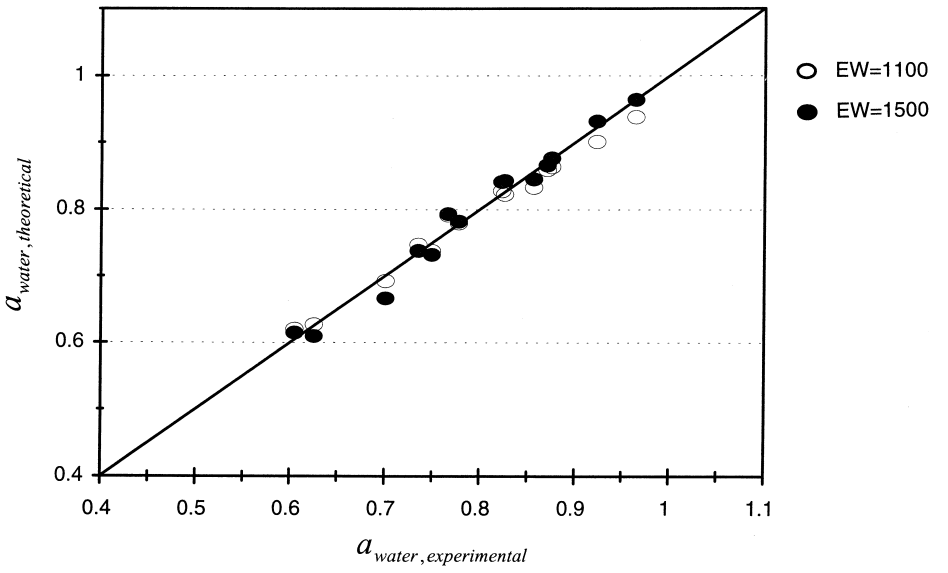

Fig. 6. Comparison of theoretical and experimental water activity in sulfonic DuPont membranes at 90°C.

DuPont membrane with $EW_{dry} = 1.50$, there were considerable discrepancies between the predicted results of the Pitzer model and the experimental results. This was expected because it is unlikely that the shielding of the fixed charged groups from the other dissolved ions in the membrane is identical for membranes with different equivalent weights. By multiplying the molality of the membrane (see relation 3) in the Pitzer relations with a shielding factor of $f_{shielding} = 0.33$, a good agreement was obtained between the results predicted by the Pitzer model and the experimental data for the sulfonic DuPont membrane with $EW_{dry} = 1.50$ (see closed points in Figs. 4–6). It should be emphasized that $f_{shielding}$ as used in this work is a scale factor and does not give the absolute value of the shielding, because the sulfonic DuPont membrane with $EW_{dry} = 1.10$ was given an arbitrary shielding factor of 1.

6. Conclusions

In this work, the application of the Pitzer model to electrolytes present in a membrane has been discussed. First, it was shown that the Pitzer model can successfully be used to predict the mean activity coefficients of NaCl and NaOH solutions, which are of interest to the chloralkali industry. Hereafter, the Pitzer model was applied to experimentally obtained sorption data for a sulfonic DuPont membrane with an EW_{dry} of 1.10 and 1.50 in order to determine the Pitzer interaction coefficients describing the interaction between the fixed charged groups of the membrane and the dissolved ions. In the application of the Pitzer model to the membrane, it was assumed that the fixed charged groups of the membrane are ‘ordinary’ ions in the aqueous solution in the membrane. It was

shown that the Pitzer model can be used to predict the experimental sorption data, provided the molality of the membrane, as used in the Pitzer relations, is multiplied by a constant representing a shielding term. This shielding term is a scaling factor depending on the equivalent weight and had to be incorporated in the optimization procedure of the Pitzer parameters. The sulfonic DuPont membrane with $EW_{dry} = 1.10$ was given an reference $f_{shielding} = 1$, while for the sulfonic DuPont membrane with $EW_{dry} = 1.50$ the shielding factor was equal to $f_{shielding} = 0.33$.

7. List of symbols

A_ϕ	Interaction parameter Pitzer model (−)
B, B', B^ϕ	Interaction parameter Pitzer model (−)
b	Interaction parameter Pitzer model (−)
C, C^ϕ	Interaction parameter Pitzer model (−)
EW_{dry}	Equivalent weight (kg/mol)
e	Water uptake (−)
F	Faraday constant (96487 C/mol) (C/mol)
$f_{shielding}$	Shielding factor (−)
f^γ	Interaction parameter Pitzer model (−)
I	Ionic strength (mol/kg)
M_i	Molecular weight of component i (kg/mol)
m_i	Molality of component i (mol/kg)
n	Total number of components (−)
T	Temperature (K)
Z	Modified ionic strength (mol/kg)
z_i	Ionic charge of component i (−)

Greek

α_1, α_2	Interaction parameter Pitzer model (−)
$\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$	Interaction parameter Pitzer model (−)
γ_i	Activity coefficient of component i (−)
$\gamma_\pm$	Mean activity coefficient (−)
φ	Potential (V)
μ_i	Electrochemical potential of component i (J/mol)
ν_i	Stoichiometric coefficient of component i (−)
ρ	Density (kg/m^3)
Φ, Φ', Φ^ϕ	Interaction parameter Pitzer model (−)
$\phi_{osmotic}$	Osmotic coefficient (−)
Ψ	Interaction parameter Pitzer model (−)

Sub / superscript / miscellaneous

i, j	Component index
n	nth component
—	Property in the membrane phase

Appendix A. Pitzer model

The Pitzer equations for the osmotic coefficient φ, the activity coefficient of a cation M (γ_M), the activity coefficient of an anion X (γ_X) are as follows:

$$(\varphi_{\text{osmotic}} - 1) = \frac{2}{\sum_i m_i}\left[\frac{-A_\phi I^{3/2}}{(1+bI^{1/2})} + \sum_c\sum_a m_c m_a\left(B^\phi_{ca} + ZC_{ca}\right)\right.$$
$$\left. + \sum_{c<c'}\sum m_c m_{c'}\left(\Phi^\phi_{cc'} + \sum_a m_a \psi_{cc'a}\right) + \sum_{a<a'}\sum m_a m_{a'}\left(\Phi^\phi_{aa'} + \sum_c m_c \psi_{caa'}\right)\right] \quad \text{(A1.1)}$$

$$\ln(\gamma_M) = z_M^2 F + \sum_a m_a(2B_{Ma} + ZC_{Ma}) + \sum_c m_c\left(2\Phi_{Mc} + \sum_a m_a \psi_{Mca}\right)$$
$$+ \sum_{a<a'}\sum m_a m_{a'}\psi_{Maa'} + z_M \sum_c\sum_a m_c m_a C_{ca} \quad \text{(A1.2)}$$

$$\ln(\gamma_X) = z_X^2 F + \sum_c m_c(2B_{cX} + ZC_{cX}) + \sum_a m_a\left(2\Phi_{Xa} + \sum_c m_c \psi_{cXa}\right)$$
$$+ \sum_{c<c'}\sum m_c m_{c'}\psi_{cc'X} + |z_X|\sum_c\sum_a m_c m_a C_{ca} \quad \text{(A1.3)}$$

The summations in Eqs. (A1.1), (A1.2) and (A1.3) over c and a respectively are summations over the cations and the anions respectively present in the solution. The various terms in Eqs. (A1.1), (A1.2) and (A1.3) are defined as follows:

$$I = 1/2\sum_i m_i z_i^2 \quad \text{(A1.4)}$$

$$Z = \sum_i m_i |z_i| \quad \text{(A1.5)}$$

$$F = f^\gamma + \sum_c\sum_a m_c m_a B'_{ca} + \sum_{c<c'}\sum m_c m_{c'}\Phi'_{cc'} + \sum_{a<a'}\sum m_a m_{a'}\Phi'_{aa'} \quad \text{(A1.6)}$$

Table 5
Mixture independent parameters of the Pitzer model

Parameter	Numerical value
A_ϕ [(kg/mole)$^{1/2}$]	0.3915 (25°C)
A_ϕ [(kg/mole)$^{1/2}$]	0.4491 (90°C)
b [(kg/mole)$^{1/2}$]	1.2
α_1 [(kg/mole)$^{1/2}$]	2.0
α_2 [(kg/mole)$^{1/2}$]	0.0
$\Phi'_{cc'}$ or $\Phi'_{aa'}$ [kg/mole]	0.0

N.B.: 1. α_1 and α_2 are different for 2-2 electrolytes: $\alpha_1 = 1.4$ (kg/mole)$^{1/2}$ and $\alpha_2 = 12$ (kg/mole)$^{1/2}$.
2. In general, the term Φ' is set equal to 0.

Table 6
Mixture dependent parameters of the Pitzer model

Parameter
$\beta^{(0)}$
$\beta^{(1)}$
$\beta^{(2)}$ (often equal to zero)
C^{ϕ}
$\Phi_{cc'}$ or $\Phi_{aa'}$
$\psi_{cc'a}$ or $\psi_{caa'}$

$$f^{\gamma} = -A_{\phi}\left[\frac{I^{1/2}}{1+bI^{1/2}} + \frac{2}{b}\ln(1+bI^{1/2})\right] \tag{A1.7}$$

$$B_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX}\, g\left(\alpha_1 I^{1/2}\right) + \beta^{(2)}_{MX}\, g\left(\alpha_2 I^{1/2}\right) \tag{A1.8}$$

in which:

$$g(x) = 2\left[1-(1-x)e^{-x}\right]/x^2 \tag{A1.9}$$

$$B'_{MX} = \beta^{(1)}_{MX}\, g'\left(\alpha_1 I^{1/2}\right) + \beta^{(2)}_{MX}\, g'\left(\alpha_2 I^{1/2}\right). \tag{A1.10}$$

in which:

$$g'(x) = -2\left[1-\left(1+x+1/2\,x^2\right)e^{-x}\right]/x^2 \tag{A1.11}$$

Table 7
Interaction parameters $\beta(0)$, $\beta(1)$, $\beta(2)$ and C^{φ}

Na^+	$\beta(0)$	$\beta(1)$	$\beta(2)$	C^{φ}
Cl^-	0.0765	0.2664	0	0.00127
OH^-	0.0864	0.253	0	0.0044
SO_4^{2-}	0.09886	1.32469	0	−0.01052
Sulfonic	0.07031	−11.0268	0	−0.00362

Table 8
Interaction parameter $\Phi_{aa'}$

	SO_4^{2-}	OH^-	Cl^-
Sulfonic	−	0.17011	0.28584
Cl^-	0.030	−0.050	
OH^-	−0.013		
SO_4^{2-}			

Table 9
Interaction parameter $\psi_{aa'c}$

	Na^+
Cl^-/OH^-	−0.006
Cl^-/SO_4^{2-}	0.000
Cl^-/sulfonic	−0.04446
OH^-/SO_4^{2-}	−0.009
OH^-/sulfonic	−0.01134

$$B^{\phi}_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX}\exp\left(-\alpha_1 I^{1/2}\right) + \beta^{(2)}_{MX}\exp\left(-\alpha_2 I^{1/2}\right) \tag{A1.12}$$

$$C_{MX} = \frac{C^{\phi}}{2|z_M z_X|^{1/2}} \tag{A1.13}$$

$$\Phi^{\phi}_{cc'} = \Phi_{cc'} + I\Phi'_{cc'} \tag{A1.14}$$

So far, a few parameters in Eqs. (A1.1), (A1.2), (A1.3), (A1.4), (A1.5), (A1.6), (A1.7), (A1.8), (A1.9), (A1.10), (A1.11), (A1.12), (A1.13) and (A1.14) have not been defined. These parameters are the mixture independent and the mixture dependent parameters. In Table 5 the mixture independent parameters are summarized. The mixture dependent parameters have been included in Table 6. For many systems, these parameters have been tabulated in literature [1] and are for the systems studied summarized in Appendix B.

Appendix B. Interaction parameters Pitzer model

The mixture dependent parameters are given in Tables 7–9. All parameters are valid for 90°C. The data without a mark originate from the work of Pitzer [1]. The data marked with (1) originate from the present work, while the data marked with (2) were taken from Lobo [5]. All data without a mark or

Table 10
Temperature derivative $\beta(0)$, $\beta(1)$, $\beta(2)$ and C^{φ}

	Temperature derivative Na^+/OH^-	Temperature derivative Na^+/Cl^-
$\beta(0)$	7.00×10^{-4}	7.15×10^{-4}
$\beta(1)$	1.34×10^{-4}	7.00×10^{-4}
$\beta(2)$	–	–
C^{φ}	-1.89×10^{-4}	-1.05×10^{-4}

For calculations at temperatures other than 298.15, the following correction has to be applied: Parameter (T) = Parameter (298.15 K) + Temperature derivative $(T-298.15)$.

marked with a 2 are valid for 25°C. The data marked with a 1 are valid for 90°C. The Pitzer parameters $\beta(0)$, $\beta(1)$, $\beta(2)$ and C^{φ} at 90°C can be calculated using the temperature derivatives for $\beta(0)$, $\beta(1)$, $\beta(2)$ and C^{φ} as given by Pitzer (see Table 10).

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